thioether bond used to hold the quinone onto oligonucleotide **3**.

If the most nucleophilic atom (guanine N7) of DNA had been derivatized to form the cross-link, then strand scission at the site of modification should have been induced under alkaline conditions.[13] No such fragmentation was noted. Instead, covalent attachment between strands was reversed. Treatment with triethylamine or piperidine (90 °C) transformed the cross-linked duplex back to a species migrating in a manner similar to **4** (Figure 2B). In addition, a related conversion was unavoidable during the purification of the photochemical product and this decomposition is evident in lanes 5 and 6 of Figure 2B.

Finally, Becker and Wang[14] had shown that a protocol using sodium borohydride would cleave the DNA backbone at a thymine or cytosine with a saturated C5–C6 bond. A similar analysis performed on the cross-linked material described here was insufficient to cause scission at the site of modification. The surprising profile of this quinone-based photoalkylation might then suggest that an equally unusual bond reorganization occurred during irradiation. This process would likely include the formation of at least one new carbon–carbon bond and may be reminiscent of a previously characterized dimerization of naphthoquinones.[15]

Although covalent cross-linking between DNA and free methyl-1,4-naphthoquinone had not been previously detected after photolysis, such a reaction can be induced when the quinone is forced to remain in close proximity to a target sequence of DNA. This alkylation immortalizes the hybridization of a DNA probe and may be expected to serve as a basis for future protocols in nucleic acid manipulation. Whether or not other species may also form distinct products when forced to surround DNA remains to be demonstrated.

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Supplementary Material Available: Preparation of oligonucleotides and the syntheses of **1**–**3** (2 pages). Ordering information is given on any current masthead page.

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Carbenes and the O–H Bond: Spectroscopic Evidence for Protonation of Diarylcarbenes To Give Diarylcarbenium Ions

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The reaction of diarylcarbenes with O–H bonds[1] plays a central and critical role in the assignment of chemical and physical properties to specific spin states. The interpretation of absolute rates[2] suffers from mechanistic ambiguity. About 30 years ago we suggested, on the basis of indirect evidence, that diphenylcarbene abstracts a proton from alcohols to form the diphenylcarbenium ion,[3] eq 1, path a. On the other hand, Bethell et al., studying thermal reactions of diphenyldiazomethane with ROH and their isotope effects, favored the electrophilic attack of diphenylcarbene on the oxygen atom,[4] eq 1, path b.

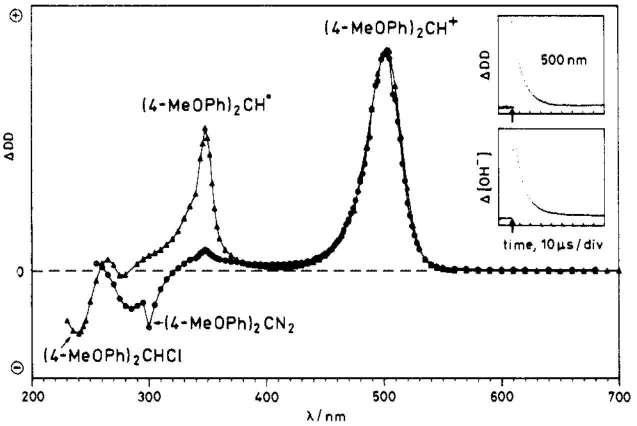
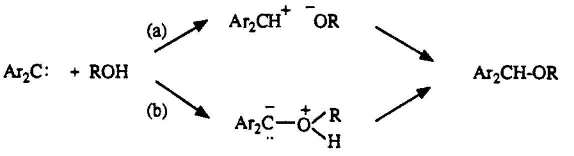


Figure 1. Changes in optical density (OD) observed on 248-nm photolysis of 0.9 mM $(4\text{-MeOC}_6H_4)_2CN_2$ in acetonitrile containing 2% of water (v/v), circles (measured at 40 ns after the pulse), and of 0.13 mM $(4\text{-MeOC}_6H_4)_2CHCl$ in acetonitrile containing 0.2 M CH_2Cl_2, triangles (recorded at 1.6 µs). The spectra were normalized to give the same OD at 500 nm. The radical $(4\text{-MeOC}_6H_4)_2CH^•$ originates from H abstraction from the solvent by the triplet carbene and from photohomolysis of the chloride, respectively. Insets: Comparison of the decay of Ar_2CH^+, monitored at 500 nm (upper inset), with the decrease of conductance (lower inset), due to neutralization of HO^- by H^+ from the (rate-determining) reaction of Ar_2CH^+ with H_2O. The cation was produced by LFP of 0.12 mM $(4\text{-MeOC}_6H_4)_2CN_2$ in acetonitrile–water, 1:2 (v/v), containing 1 mM NaOH. Note: In this particular figure Ph represents C_6H_4.



(1)

Product and label distributions have revealed protonation of 7-norbornenylidenes,[5] (benzo)cycloheptatrienylidenes,[6] cyclopentenylidenes,[7] and arylbenzylcarbenes.[8] Analogous techniques are not applicable to diarylcarbenes. The reactivities of alcohols toward diphenylcarbene were found to parallel their acidity.[4,9] The kinetic range, however, was much smaller than that observed for typical nucleophilic carbenes.[10] In this communication we report the spectroscopic detection of diarylcarbenium ions, following the generation of diarylcarbenes by laser flash photolysis (LFP) in protic solvents.

Diarylcarbenium ions have recently become accessible for time-resolved measurements by heterolytic photocleavage of Ar_2CHX.[11-17] The data thus gathered are used in the present

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Table I. Characteristics of Diarylcarbenium Ions

substituents			via diarylcarbenes			via photoheterolysis		
4-	4′-	solvent	precursor	λ_{max}, nm	k,[a] s^{-1}	precursor	λ_{max},[f] nm	k,[g] s^{-1}
MeO	MeO	AN–W[e] (1:2)	Ar_2CN_2	500	$(1.2 \pm 0.1) \times 10^5$	Ar_2CHOAc	500	1.3×10^5
MeO	H	AN–W (1:4)	Ar_2CN_2	455	$(2.3 \pm 0.1) \times 10^6$	Ar_2CHOAc	455	2.1×10^6
Me	Me	AN–W (1:2)	Ar_2CN_2	462	$(4.2 \pm 0.1) \times 10^7$	Ar_2CHOAr[c]	460	3.2×10^7
H	H	TFE[d]	tetraphenyl oxirane	435	$(3.2 \pm 0.1) \times 10^6$	Ar_2CHOAr[c]	440	3.2×10^6
		AN–TFE (1:1.6)	Ar_2CN_2	430	$(6.6 \pm 0.2) \times 10^6$	Ar_2CHCl	435[e]	6.8×10^6
Cl	Cl	AN–TFE (1:1.6)	Ar_2CN_2	470	$(5.9 \pm 0.1) \times 10^6$	Ar_2CHCl	472[e]	7.0×10^6

[a] At 20 ± 2 °C. [b] Acetonitrile–water. [c] OAr = 4-cyanophenyl ether. [d] 2,2-Trifluoroethanol. [e] In acetonitrile. [f] References 11 and 17. [g] Reference 11 and 13.

work to identify the transients derived from diarylcarbene precursors. LFP (248 nm, 20-ns pulses) of 4,4′-dimethoxydiphenyldiazomethane in acetonitrile–water gave rise to virtually the same transient absorption as that obtained by photoheterolysis of Ar_2CHX[11,13,17] (Figure 1 and Table I). The decay of the transient was first-order, the rate constant being unaffected by oxygen and independent of the precursor concentration. Corroboration was provided by the use of time-resolved conductivity detection in weakly basic solution. The observed steep increase in conductance after the pulse (Figure 1) is due to protonation of the carbene by H_2O to give the carbenium ion and OH^-. The subsequent decrease in conductance is caused by reaction of the cation with the solvent, neutralizing OH^-. LFP of 4-methoxy- and 4,4′-dimethyldiphenyldiazomethane in acetonitrile–water also generated diarylcarbenium ions whose absorption and reactivity were in good agreement with previous measurements[11,13] (Table I).

The reaction rate of the parent diphenylcarbenium ion is too fast to be measured in acetonitrile–water but is conveniently monitored in the less nucleophilic solvent 2,2,2-trifluoroethanol (TFE). The acidity of TFE ($pK_a = 12.4$), however, induces decomposition of diphenyldiazomethane. Therefore, solutions of diphenyldiazomethane in acetonitrile were mixed with TFE in a flow system ca. 10 s prior to LFP. Tetraphenyloxirane, unaffected by TFE, was used as an alternative source of diphenylcarbene.[18] The transient spectra and rates thus obtained identify the diphenylcarbenium ion unambiguously. 4,4′-Dichlorodiphenylcarbenium ion was generated similarly from the analogous diazo compound (Table I).

Diarylcarbenium ions covering a reactivity range (with water) of 10^7 have thus been shown to arise from carbenic precursors by protonation with OH groups. In contrast, LFP of 9-diazofluorene in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) did not provide the transient spectrum of 9-fluorenyl cation[14] (which is readily observed following LFP of 9-fluorenol in HFIP).[19] In analogy with cyclopentadienylidene,[7] and in accordance with the low basicity of its "aromatic" singlet state, 9-fluorenylidene is not protonated by a solvent as acidic as HFIP ($pK_a = 9.3$).

In all successful experiments, the absorption spectra of diarylcarbenium ions evolved within the 20-ns laser pulse. Rapid formation of the carbocations is consistent with the rates (10^9–10^{10} M^{-1} s^{-1}) at which singlet diphenylcarbene is quenched by ROH.[10,20] Possible alternatives will be briefly considered: (i) Protonation of photoexcited diazo compounds might give diazonium ions and hence carbocations. As a consequence of this process, the quantum yields of photodecomposition in protic solvents should exceed those in aprotic solvents, which is not observed.[3] Our results with tetraphenyloxirane and 9-diazofluorene also argue against this mechanism. (ii) Photoexcitation of triplet carbenes might lead to excited triplet states which are known to behave very much like singlets.[21-24] The yield of carbocation was found to increase linearly with the intensity of the laser pulse. Thus one photon is sufficient to generate the carbocation precursor whereas two photons would be required to obtain the excited triplet state.

In summary, our data strongly support the protonation of singlet diarylcarbenes by ROH (eq 1, path a), a process that can compete efficiently with intersystem crossing to the triplet state.

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Easy, Reversible Addition of Mercury to Triplatinum Clusters: A Model for the First Step in Amalgamation of Platinum

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The interaction of mercury atoms with metal surfaces is important, but it is difficult to study with most metals, including Pt, because of the ease of amalgamation.[1] Since there is a remarkable resemblance between the ways in which small molecules bind to the coordinatively unsaturated cluster complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ (**1**), dppm = $Ph_2PCH_2PPh_2$, and a Pt(111) surface,[2] a study of mercury coordination to **1** should be a useful model for chemisorption of mercury atoms on a platinum surface which leads to PtHg amalgam. There has been theoretical work on $(Pt_3(CO)_6Hg)_\infty$ polymers,[3] which are predicted to have interesting physical properties, and of several known compounds with PtHg bonds,[4] the complexes $[\{Pt_3(\mu\text{-}L)_3L_3\}_2Hg]$, L = 2,6-

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